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Acid Catalyzed Carbonylation of Chloromethyl Methyl Ether

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The carbonylation of chloromethyl methyl ether by carbon monoxide in the presence of Lewis acid has been investigated. It has been found to be an equilibrium reaction, and the yield of the carbonylation product depended upon the pressure of carbon monoxide. With BF_3 catalyst, the equilibrium constant at 10°C was obtained as 2.77 l/mol. From the temperature dependency of the equilibrium constants, the change of enthalpy in the reaction was calculated to be −7.2 kcal/mol.

KEY WORDS: Carbonylation/ Carbon monoxide/ Methyl methoxyacetate/ Lewis acid/ Heat of reaction/

INTRODUCTION

Chloromethyl methyl ether (CMME), which is a useful reagent for methylation, chloromethylation, methoxymethylation and esterification, is easily synthesized from formaldehyde, methanol and hydrochloric acid.[1]

$$CH_2O+CH_3OH+HCl \rightarrow CH_3OCH_2Cl+H_2O$$

Both formaldehyde and methanol are known as the principal materials in C_1 chemistry, then CMME can be regarded as one of the C_1 chemicals.

Methoxyacetyl chloride, carbonylation product of CMME, is easily decomposed by water or methanol to afford methoxyacetic acid or methyl methoxyacetate.

$$CH_3OCH_2Cl+CO \rightarrow CH_3OCH_2COCl \begin{cases} \xrightarrow{H_2O} CH_3OCH_2COOH+HCl & (1) \\ \xrightarrow{CH_3OH} CH_3OCH_2COOCH_3+HCl & (2) \end{cases}$$

This acid or ester can be led to methoxyethanol and also to ethylene glycol by reduction and hydrolysis.

$$CH_3OCH_2COOCH_3 \rightarrow CH_3OCH_2CH_2OH \rightarrow HOCH_2CH_2OH$$

Direct synthesis of ethylene glycol is one of the most important themes in C_1 chemistry and has been widely investigated.[2] Synthetic methods of glycolic acid, methoxyacetic acid and their derivertives from formaldehyde have been also explored.[3] Thus, the carbonylation of CMME has a significant value.

CMME is a substituted alkyl halide. The carbonylation of organic halides using transition-metal catalysts has been enormously studied.[4] It has been revealed

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that a electron-donating substituent in halides restrains the rate of oxidative addition of halides to metals.[5] Then, alkyl halides having methoxy group such as CMME are unfavorable for the carbonylation using transition-metal catalysts. Moreover, in the metal-catalyzed carbonylation of halides, addition of a base as a acceptor of liberated hydrogen halides is essential, but there are many cases in which organic bases react with the substrates. As CMME also reacts immediately with weak organic bases such as 2,6-lutidine, catalytic carbonylation of CMME using transition -metals seems to be hardly possible.

In this paper, the carbonylation of CMME using Lewis acid will be reported. CMME is decomposed by water or methanol.

$$CH_3OCH_2Cl+H_2O \longrightarrow CH_3OH+CH_2O+HCl \quad (4)$$

$$CH_3OCH_2Cl+CH_3OH \longrightarrow CH_3OCH_2OCH_3+HCl \quad (5)$$

Then, water or alcohols could not be used as the solvent. Reactions were carried out under the conditions without a solvent or with several inert solvents. Lewis acids, $ZnCl_2$ and BF_3, were used as catalyst.

EXPERIMENTAL

Materials. CMME was obtained from Tokyo Kasei Co. (purity: above 95%) and used without further purification. All solvents were dried by the usual method. Tetrahydrofuran was dried with Na metal and distilled. Carbon monoxide was prepared in our laboratory (purity: above 98%). BF_3 was purchased from Hashimoto Kasei Co..

Procedure. Reactions were carried out in a rocking type stainless-steel autoclave (50 ml). In the $ZnCl_2$-catalyzed reactions, the catalyst, solvent and CMME were put into the autoclave. The air in the autoclave was purged with CO several times, and then CO was charged up to the desired pressure. The autoclave was heated to the reaction temperature, and rocking was started. This time was taken as the beginning of the reaction. In the reaction with BF_3 catalyst, the autoclave containing CMME and a solvent was flushed with nitrogen or argon gas, and then BF_3 was introduced into the autoclave cooled in an ice bath. The autoclave was shaken to enhance the dissolution of the gas. The amount of dissolved BF_3 was estimated from the pressure drop of BF_3 gas in the reservoir of known volume. Then CO gas was charged, and the reaction was started. After a certain reaction period, the rocking was stopped, and the autoclave was cooled. Methanol for solvolysis was injected into the autoclave by means of a high pressure plunger pump, thus the carbonylation product and the unreacted CMME were converted to the ester (Eq. 2) and dimethoxymethane (Eq. 5), respectively. Analysis was performed by means of GLC with an internal standard.

RESULTS AND DISCUSSION

Products in the reaction mixture treated with methanol were methyl methoxyacetate as a carbonylation product, and dimethoxymethane as a decomposition pro-

duct of CMME. When the reaction mixture was hydrolyzed, methoxyacetic acid and methanol were detected. Other products such as chloromethyl acetate and methyl chloroacetate, which should be formed by the insertion of carbon monoxide into the carbon-oxygen bonds of CMME, were not detected. This suggests that the catalysts would not combine with oxygen atom, but with halogen atom of CMME.

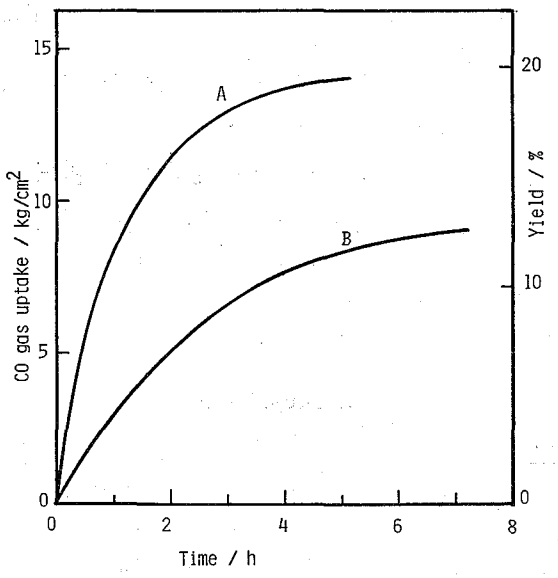

Fig. 1. CO gas uptake in the $ZnCl_2$ catalyzed reaction. [CMME]=131 mmol, [$ZnCl_2$]=22 mmol, without solvent, temp.=40°C, Curve A: P_{co}=260 kg/cm², Curve B: P_{co}=150 kg/cm².

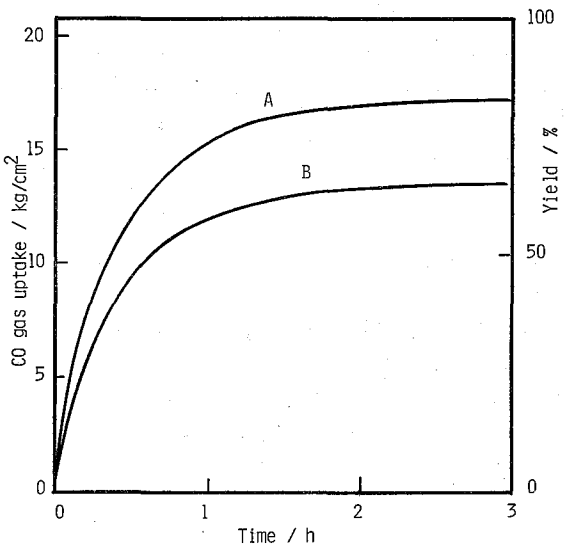

Fig. 2. CO gas uptake in the BF_3 catalyzed reaction. [CMME]=40 mmol, [BF_3]=40 mmol, solvent: 1,2-dichloroethane (10 ml), temp.=10°C, Curve A: P_{co}=300 kg/cm², Curve B: P_{co}=150 kg/cm².

$$CH_3OCH_2Cl\cdots MX_n \quad (M: Zn \text{ or } B,\ X: Cl \text{ or } F)$$

$ZnCl_2$ catalyst: Typical gas uptake curves in the reaction using $ZnCl_2$ catalyst are shown in Fig. 1. The total amount of CO gas uptake fairly agreed with the amount of the ester determined by GLC. The reaction did not complete even after a sufficiently long reaction period, but approached an equilibrium as seen in Fig. 1.

Non-polar organic compounds are poor solvents for $ZnCl_2$. CMME can dissolve a little amount of the catalyst. Thus the rates of the reactions using $ZnCl_2$ were generally slow. The results obtained were summarized in Table 1, where in all runs except Runs 6, 8 and 9, the catalyst remained partly undissolved.

$ZnCl_2$ dissolved a little more into benzonitrile-CMME mixture than into a pure CMME. The ester yield by the reaction in benzonitrile solvent increased a little in comparison with that in a pure CMME (Runs 4 and 2).

Though tetrahydrofuran well dissolved $ZnCl_2$, the ester yield was low. It may be due to rather strong interaction of $ZnCl_2$ with the solvent (Run 6).

$ZnCl_2$ was sparingly soluble in 1,2-dichloroethane, so this solvent did not improve the yield of the ester (Run 7).

Despite the incomplete dissolution of $ZnCl_2$, there were some cases in which the amount of the ester exceeded that of charged $ZnCl_2$ (TON>1: Runs 1, 3 and 4). This indicates that free methoxyacetyl chloride and $ZnCl_2$ were released from the acyl chloride-catalyst complex.

$$[CH_3OCH_2COCl\cdots ZnCl_2] \rightleftarrows CH_3OCH_2COCl + ZnCl_2$$
$$\text{or} \quad [CH_3OCH_2CO^+]ZnCl_3^-$$

Table 1 $ZnCl_2$ catalyzed carbonylation of CMME

Run	$[CMME_2]_0$ /mmol	$[ZnCl_2]_0$ /mmol	Solvent[a] (ml)	Time /h	Yield[b] /%	T.O.N[c]
1	197.0	5.2	——[d]	7	15.6	5.93
2	131.2	22.5	——[d]	7	12.8	0.74
3[e]	131.2	22.3	——[d]	5	17.3	1.03
4	133.0	22.6	BN(5)	5	19.9	1.17
5	66.5	22.2	BN(10)	5	16.8	0.50
6	66.5	22.1[f]	THF(10)	5	10.9	0.33
7	66.4	24.1	DCE(10)	6	11.9	0.33
8	131.2	22.0[f]	MET(3)	8[g]	23.0	1.34
9	61.6	39.0[f]	DMM(10)	9[g]	101.0	1.60

P_{CO}=150 kg/cm² except Run 3, reaction temp.=40°C

a) Solvent: BN=benzonitrile, THF=tetrahydrofuran, DCE=1,2-dichloroethane, MET=methanol, and DMM=dimethoxymethane.

b) Yield of the ester based on $[CMME]_0$.

c) Molar ratio of produced ester to charged catalyst.

d) Reaction without solvent.

e) P_{CO}=250kg/cm².

f) Catalyst was dissolved completely. In other runs, catalyst remained partly undissolved.

g) CO gas uptake did not stop within this reaction period.

The complexes of alkyl halides with $AlCl_3$ have been suggested to have a polarized character.[6]

$$R-X+AlCl_3 \rightleftarrows [R^{+\delta}X^{-\delta}\cdot AlCl_3]$$

In the present case of CMME with $ZnCl_2$, a polarized complex such as $[CH_3OCH_2^{+\delta}Cl^{-\delta}\cdot ZnCl_2]$ is reasonable. On the other hand, concerning the character of the complex between methoxyacetyl chloride and $ZnCl_2$, both ionic and polarized character are conceivable, because the complex of acetyl chloride with $AlCl_3$ has been reported to be a mixture of an ionic complex $[CH_3CO^+]AlCl_4^-$ and a non-ionic complex $[CH_3COCl\cdot AlCl_3]$.[7]

As mentioned above, methanol decomposes CMME easily as Eq. 5. But the solubility of $ZnCl_2$ into methanol is large. The effects of addition of methanol were examined (Run 8). The ester yield increased, and the CO gas uptake did not cease even after 8 hours. As the decomposition of CMME is very fast,[8] dimethoxymethane, instead of methanol, must exist in this reaction system before charging CO gas. Dimethoxymethane itself did not react with CO in the presence of $ZnCl_2$. Therefore, it may act as a reagent for the solvolysis of the produced acyl chloride complex, and reproduce CMME.

$$\begin{matrix}[CH_3OCH_2COCl\cdots ZnCl_2] \\ \text{or}\quad [CH_3OCH_2CO^+]ZnCl_3^-\end{matrix} + CH_3OCH_2OCH_3 \longrightarrow CH_3OCH_2COOCH_3 + CH_2OCH_2Cl + ZnCl_2$$

This becomes clear by the fact that the ester yield using dimethoxymethane solvent exceeded 100% after 9 hours, and yet the gas uptake did not cease at this time (Run 9). Consequently, methanol or dimethoxymethane was an inadequate solvent for the carbonylation of CMME.

BF_3 catalyst: In both cases using 1,2-dichloroethane as a solvent and without a solvent, the absorption of BF_3 occured immediately up to the equivalent amount to CMME. This means that the formation of 1:1 complex was completed in a short period.

$$CH_3OCH_2Cl+BF_3 \longrightarrow [CH_3OCH_2^{+\delta}Cl^{-\delta}\cdot BF_3]$$

It has been suggested that the complex of CMME with BF_3 has a polarized character, not an ionic one.[9] On the other hand, it has been confirmed that the complex between acetyl fluoride and BF_3 has an ionic character.[10] Thus, an ionic species is feasible for the complex of the carbonylation product of CMME.

$$[CH_3OCH_2^{+\delta}Cl^{-\delta}\cdot BF_3]+CO \rightleftarrows [CH_3OCH_2CO^+]BF_3Cl^-$$

Table 2 shows the results obtained using BF_3 catalyst. As shown in Fig. 2, the BF_3-catalyzed reaction was much faster than that in $ZnCl_2$-catalyzed reaction. Especially at 40°C, the reactions reached their equilibrium within 1 hour (Runs 1, 2, 4, 5 and 6), except for the case of low BF_3 concentration at which it took 2 hours until the reaction reached its equilibrium (Run 3).

When diethyl ether was used as a solvent, the carbonylation of CMME scarecely occured due to rather strong interaction of BF_3 with the solvent than with CMME (Run 4). 1,2-dichloroethane as a solvent did not particularly affect the yield of the

Table 2. BF_3 catalyzed carbonylation of CMME

Run	$[CMME]_0$ /mmol	$[BF_3]_0$ /mmol	Solvent[a] (ml)	Temp. /°C	Time[b] /h	Yield[c] /%	T.O.N[d]
1	66.7	60.6	——[e]	40	5	41.6	0.457
2	133.8	93.3	——[e]	40	6	36.2	0.520
3	133.5	15.0	——[e]	40	3.5	14.5	1.29
4	66.8	83.7	DEE(10)	40	5	0.5	0.004
5	64.6	52.2	DCE(10)	40	6	37.2	0.460
6	39.9	40.7	DCE(10)	40	2	41.2	0.404
7	40.4	38.4	DCE(10)	19	3	57.8	0.608
8	40.4	40.8	DCE(10)	10	5	66.0	0.654
9	40.4	60.0	DCE(10)	10	8	65.4	0.440
10	40.4	23.0	DCE(10)	10	5	53.8	0.946
11	40.4	17.1	DCE(10)	10	7	43.2	1.00
12	40.4	10.1	DCE(10)	10	8	23.8	0.952
13	40.4	7.5	DCE(10)	10	7[f]	12.1	0.653

P_{CO}=150 kg/cm^2

a) Solvent: DEE=diethyl ether, DCE=1,2-dichloroethane.

b) Except for Runs 4 and 13, the reactions reached an equilibrium within 1 hour in Runs 1, 2, 5, 6 and 7, within 2 hours in Run 3, within 3 hours in Run 8, within 5 hours in Runs 10, 11 and 12, and within 8 hours in Run 9.

c) Yield of the ester based on $[CMME]_0$.

d) Molar ratio of the produced ester to charged BF_3.

e) Reaction without solvent.

f) CO gas uptake did not stop within this reaction period.

ester (Runs 1 and 5).

In contrast with the case of $ZnCl_2$, the reaction using BF_3 proceeded only to the extent of the corresponding amount of BF_3 even when the concentration of BF_3 was lowered (Runs 10–12). This suggests no occurrence of liberation of free BF_3 and methoxyacetyl chloride from the acyl chloride complex.

$$[CH_3OCH_2CO^+]BF_3Cl^- \not\rightarrow CH_3OCH_2COCl + BF_3$$

In Run 13, the amount of the ester was lower than that of BF_3 in spite of the condition of lower BF_3 concentration. This is due to the incomplete reaction as the gas uptake still continued at the end of this reaction period.

On the other hand, when excess BF_3 was added to CMME, the yield of the ester was not almost varied, but the rate of the reaction became so slow that it took 8 hours to reach its equilibrium. An additional interactoin of excess BF_3 to oxygen of the ether complex may cause the suppression of the nucleophilic attack of CO.

The ester yield at the equilibrium depended upon the pressure of CO (Table 3). In the following overall reaction,

$$\begin{array}{ccc} & CO(g) & \\ & \downarrow\uparrow \quad K' & \\ CH_3OCH_2Cl + CO(l) & \rightleftarrows & CH_3OCH_2COCl \\ x_0 - a_e & & a_e \end{array} \qquad (6)$$

Table 3. Pressure effect on the equilibrium

Run	P_{CO}[a] /kg/cm^2	Yield[b] /%	$\left(\frac{a_e}{x_0 - a_e}\right)$[c]
1	40	42.3	0.733
2	56	49.2	0.968
3	83	59.3	1.46
4	130	66.0	1.94
5	175	73.3	2.75
6	247	79.2	3.81
7	270	81.8	4.49

$[CMME]_0$=40.4 mmol, $[BF_3]_0$=40 mmol, solvent: 1,2-dichloroethane, temp. =10°C, reaction time=5 h.
a) Pressure of CO at the reaction equilibrium.
b) Yield of the ester based on $[CMME]_0$.
c) See Eq. 7.

the equilibrium constant, K' is expressed as

$$K' = \left(\frac{a_e}{x_0 - a_e}\right)\frac{1}{[CO]_l} = \left(\frac{a_e}{x_0 - a_e}\right)\frac{1}{H_{co} \cdot P_{co}}, \tag{7}$$

where x_0 and a_e are the initial concentration of CMME and the equilibrium concentration of methoxyacetyl chloride, respectively, $[CO]_l$ the concentration of CO dissolved in the reaction solution, H_{co} Henry constant of CO gas, P_{co} the pressure of CO. In Eq. 7, the fugacity of CO, instead of P_{co}, should be used strictly, but under the present conditions, the correction was within 2%, then P_{co} was used.

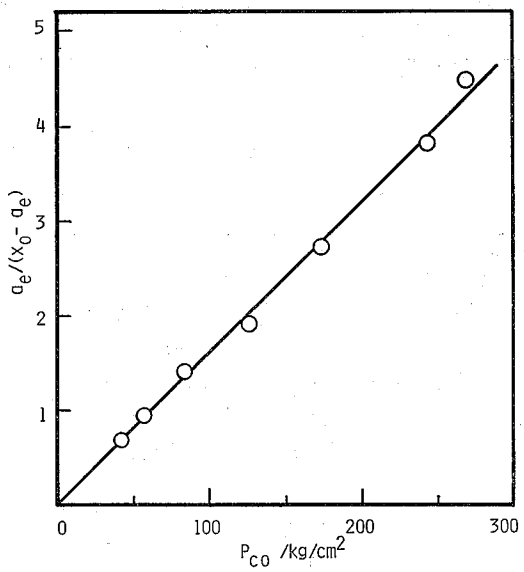

Fig. 3. Plots of $a_e/(x_0 - a_e)$ against P_{co}. Reaction conditions are given in Table 3.

Plot of $a_e/(x_0-a_e)$ against P_{co} are shown in Fig. 3. Solubilities of CO into the reaction solution under the various pressure of CO were measured, and $H_{co}=5.78\times 10^{-3}$ mol/l/atm at 10°C was obtained. From the slope of the curve in Fig. 3 and H_{co}, we obtained $K'=2.77$ l/mol at 10°C. The values of K' at 40°C and 19°C were estimated from the yields of the ester at both temperature (Runs 6 and 7 in Table 2), where the solubilities of CO were corrected approximately by the data of solubilities of CO into methanol at different temperature.[11] From the temperature dependence of the equilibrium constants, the enthalpy change in Reaction 6 was calculated to be −7.2 kcal/mol.

The formation of the complex between CMME and BF_3 is fast and completed before charging CO, so Reaction 8 lies almost to the right hand side.

$$CH_3OCH_2Cl+BF_3 \overset{K_1}{\rightleftarrows} [CH_3OCH_2^{+\delta}Cl^{-\delta}\cdot BF_3] \tag{8}$$

$$[CH_3OCH_2^{+\delta}Cl^{-\delta}\cdot BF_3]+\underset{\downarrow\uparrow}{CO(g)}\ CO(l) \overset{K_2}{\rightleftarrows} [CH_3OCH_2CO^+]BF_3Cl^- \tag{9}$$

Therefore, the heat of reaction obtained above, −7.2 kcal/mol, can be attributed mainly to Reaction 9, though this value includes the small contribution to the heat of dissolution of CO gas (~0.5 kcal/mol).

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